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(54) Title: PECTINACEOUS GELLING AGENT**(57) Abstract**

A pectinaceous gelling agent obtained from vegetable matter which contains pectinaceous substances having a degree of esterification of less than 50 %. The gelling agent contains 20 % to 50 % by weight of galacturonic acid and has a degree of esterification of 5 % to 20 %. The gelling agent may be prepared from waste vegetable matter by alkaline or acid extraction.

Pectinaceous Gelling Agent

Field of the Invention

- 5 This invention relates to a pectinaceous gelling agent which has good gelling properties, to a process for its production, and to foodstuffs containing it.

Background to the Invention

- 10 Pectins are commonly used as gelling agents in foodstuffs. Gels are tri-dimensional networks formed by the gelling agent and that contain a liquid phase. Pectin gels are formed by hydrated pectins, after physical or chemical changes that decrease the solubility of the pectins. Pectins are found in nature in the middle lamella and primary cell walls of plant tissue. They are primarily
15 straight-chained polymers of D-galacturonic acid in which the D-galacturonic acid units are linked by 1→4 glycosidic linkages. Neutral sugars such as galactose, glucose, rhamnose, arabinose and xylose may also be present; usually in the range of 5 to 10% by weight of the galacturonic acid. The rhamnose is often in the polymer as an interruption of the polygalacturonate sequences. The
20 other sugars are usually found as side chains or as contaminating polysaccharides.

- The functional group at the sixth carbon of each galacturonic acid unit may exist as a methyl ester or as a free carbonyl group. Two types of pectins are commonly distinguished on the basis of the extent of esterification of this
25 functional group. One type is low methoxy pectins which have a degree of esterification (DE) of less than 50%; that is less than 50% of the total number of functional groups exist in the methyl ester form. The other type is high methoxy pectins which have a degree of esterification (DE) of greater than 50%.

- This invention is concerned with low methoxy pectins. Low methoxy
30 pectins form gels in the presence of alkaline earth metals; especially calcium. In the gels, the galacturonic acid units making up the polymer chain are cross-linked by divalent calcium ions. Gelation and the properties of the gel however depend upon many factors including pH, temperature, the degree of esterification, molecular weight, sugar content, calcium content and pectin content.

- 35 The main sources of commercial pectin products are citrus peels and apple pomace. Lemon and orange peels are one of the richest sources. However, many

itself. However, the gelling agents of the invention contain pectinaceous substances having very low degrees of esterification; often half the degree of esterification of the pectinaceous substances in the vegetable matter itself.

5 The vegetable matter may be sunflower head and stalk residues. The pectin content of sunflower residues is about 22% by weight on a dry basis and the degree of esterification is about 15%. Preferably, when the vegetable matter is sunflower residue, the gelling agent contains about 35% to about 45% by weight of galacturonic acid and has a degree of esterification of about 5% to about 15%. Consequently gels produced using the gelling agents have excellent properties.

10 The vegetable matter may also be potato pulp, which is a waste material in the potato starch industry. The pectin content of potato pulp is about 15% by weight on a dry basis and the degree of esterification is about 17% to about 39%; generally about 30%. Preferably, when the vegetable matter is potato pulp, the gelling agent contains about 20% to about 30% by weight of galacturonic acid and has a degree of esterification of about 8% to about 18%.

In another aspect, this invention provides a process for the production of a pectinaceous gelling agent from vegetable matter that contains pectinaceous substances having a degree of esterification of less than about 50%, the process comprising:

20 subjecting comminuted vegetable matter to an acid or alkaline extraction in the presence of a sequestering agent for providing a pectinaceous extract;
 separating the extract from the vegetable matter;
 adjusting the pH of the extract to about 2 or less for causing a pectinaceous product to precipitate; and
25 neutralizing the precipitate to provide a pectinaceous gelling agent containing about 20% to about 50% by weight of galacturonic acid and having a degree of esterification of about 5% to about 20%.

For acid extraction, the comminuted vegetable matter may be suspended in an aqueous acid solution at a pH of about 3 to about 4.5. Preferably the solution
30 is at a temperature of about 60 to about 85°C.

For alkaline extraction, the comminuted vegetable matter may be suspended in an aqueous alkaline solution at a pH of about 8 to about 12. Preferably the solution is at a temperature of about 5 to about 50°C.

Preferably the sequestering agent is a polyphosphate or citrate salt; for
35 example sodium hexametaphosphate, tetrasodium pyrophosphate or sodium

For acid extraction, the extraction solution is an aqueous acid solution at a pH of about 3.0 to 4.5. The temperature is held at about 60 to 85°C. Any suitable acid may be used; for example hydrochloric acid.

For alkaline extraction, the extraction solution is an aqueous alkaline solution at a pH of about 8 to 12. The temperature is held at about 15 to 50°C; for example at room temperature. Any suitable alkaline may be used; for example sodium hydroxide.

A sequestering agent is preferably included in the acid or alkaline solution during extraction. The sequestering agent is conveniently a polyphosphate or citrate salt; preferably of a monovalent metal cation. Suitable examples sodium hexametaphosphate, tetrasodium pyrophosphate or sodium citrate. Typically, about 0.1% to about 1% by weight of the sequestering agent is used.

The extract is then separated off from the residual solid matter. This may be carried out by any suitable solid-liquid separation technique. Centrifugation is preferred. Pectinaceous matter is then caused to precipitate from the extract. This may be accomplished by adding an acid to the extract to lower the pH to about 2 or less. Any suitable alkaline may be used; for example sodium hydroxide. The precipitation is conveniently carried out at room temperature.

The precipitate is then separated from the liquid. Again any suitable solid-liquid separation technique may be used. Centrifugation is preferred. The precipitate is then neutralized to a pH of about 6 to about 7.5. This may be accomplished by suspending the precipitate in a neutral aqueous solution; for example water.

The precipitate may then be recovered, washed and dried to provide the gelling agent. Washing is preferably carried out with ethanol; for example in three stages using successively increasing concentrations. Concentrations of 70%, 80% and 95% are suitable. The drying may be carried out under vacuum at room temperature.

Alternatively, a suitable alcohol may be added to the neutral solution to cause the gelling agent to precipitate. Ethanol is a suitable alcohol. Typically, sufficient ethanol is added such that ethanol makes up at least about 50% by weight of the solution. If desired, sodium chloride may be added to the solution prior to the addition of the ethanol. The precipitate is then separated from the liquid. Again any suitable solid-liquid separation technique may be used. Centrifugation is preferred. The precipitate may then be washed and dried as before to provide the gelling agent.

lipid in the emulsion is in the range of about 2% to 15% by weight; more preferably about 5% to about 12% by weight.

If it is necessary to add carbohydrate, the carbohydrate is preferably provided in the form of a starch or flour. Suitable carbohydrate sources are wheat starch, potato starch, corn starch, wheat flour, corn flour, oat flour, rye flour, rice flour, and the like. Sugars may also be added. Typically, for chunk products, the carbohydrate, in the form of starch or flour, comprises about 3% to about 15% by weight of the gelled emulsion product.

Additional ingredients such as salts, spices, seasonings, flavoring agents, minerals, and the like may also be included in the emulsion product. The amount of additional ingredients used is preferably such that they make up about 0.5% to about 5% by weight of the emulsion product.

The emulsion product may be prepared by emulsifying the protein, carbohydrates and lipids to provide a primary emulsion. The additional ingredients such as salts, spices, seasonings, flavoring agents, minerals, and the like may be added at this time. Water may also be included in the primary emulsion to provide from about 50% to about 90% by weight of the primary emulsion. If sufficient moisture is present in the protein, especially if the protein is provided as a meat material, water need not be added. A high speed emulsifier or homogeniser is particularly suitable for preparing the primary emulsion.

The gelling agent is then added to the primary emulsion; preferably in solution. Usually between about 0.5 % and about 5% by weight of the gelling agent is suitable. If necessary a calcium source is also added; for example calcium carbonate or calcium sulfate. Preferably calcium is present in an amount of about 40 to about 150 mg/g of gelling agent used. The primary emulsion is then subjected to further mixing or emulsification. The primary emulsion is then heated to a temperature above about 65°C; for example in a mixer-cooker. Steam may be injected into the primary emulsion if desired.

If it is desired to produce chunks, the heated emulsion may then be extruded, cooled and cut into chunks. The chunks may then be mixed with a suitable gravy or jelly and filled into cans or other containers. However, if it is desired to produce a loaf type product, the heated emulsion may be filled directly into cans or other containers. The cans or other containers are then sealed and sterilized. Sterilization usually takes place at a temperature above about 120°C and for a period of at least about 15 minutes.

solution stirred for 2 hours at room temperature. The extract is then recovered using a centrifuge.

The pH of the extract is adjusted to 2.0 using 6N HCl at 25°C. The extract is stirred for 10 minutes and the stored overnight at 4°C. The precipitate which
5 forms is recovered by centrifuging at 5000 rpm for 15 minutes. The precipitate is then suspended in 5 l of water and the solution neutralized using 32% NaOH to obtain a pH of about 6.5 to 7.0. An amount of 5 l of 95% ethanol is added to the solution to cause precipitation. The precipitate is recovered by centrifuging at 5000 rpm for 15 minutes. The precipitate is then washed three times; once with
10 70% ethanol, once with 80% ethanol and once with 95% ethanol. The washed precipitate is dried in a vacuum oven at room temperature to provide a gelling agent.

Example 2 - Extraction from Sunflower Head Residues

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A) Acid extraction:- The procedure of example 1A) is repeated but using sunflower head residues instead of potato pulp. The sunflower head residues contain 5% by weight of moisture.

20

B) Alkaline extraction:- The procedure of example 1A) is repeated but using sunflower head residues instead of potato pulp. The sunflower head residues contain 5% by weight of moisture.

Example 3 - Characterization of the gelling agents

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Samples of the gelling agents of each of examples 1A, 1B, 2A and 2B are subjected to the following analysis:

- the Weibull-Stoldt method to determine fat content.
- the Kjeldahl method to determine protein content.
- 30 - hydrolysis of a 50 mg sample in 12N H₂SO₄ for 60 minutes at 30 °C and then in 0.4N H₂SO₄ for 75 minutes at 130°C. Monosaccharides are then determined using high performance anion exchange chromatography and pulsed amperometric detection.
- decarboxylation and measurement of the carbon dioxide produced to
35 determine the galacturonic acid content.

-11-

agent of example 2B, the pH is 7.1. In each case, the suspension is held at a selected hydration temperature for about 2 hours. A selected amount of a solution containing 2.9 % by weight of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is then added to obtain a desired calcium concentration. The concentration of the gelling agent is 2% by weight. The solution is then stirred for about 1 minute, poured into a mold, and stored at 4°C for 24 hours. The gelled products are then removed and subjected to analysis. In all cases, the gelling agent provides 2% by weight of the gel.

The elastic modulus E, which is a measure of gel firmness, is determined for each gelled product using a Micro System TA-XT2 Texture Analyzer. The strain applied during the measurement is 10% and the plate speed is 0.8 mm/s.

The process is repeated for the gelling agents of examples 1B and 2B but including sodium citrate during hydration.

The results are as follows:

| Sample | Hydration Temperature (°C) | Ca^{2+} Concentration (mg/g extracted product) | Sodium citrate Concentration (mM) | Elastic Modulus (Pa) |
|--------|----------------------------|---|-----------------------------------|----------------------|
| 1B | 25 | 40 | - | 42000 |
| | 25 | 40 | 8 | 15000 |
| | 25 | 100 | 8 | 24000 |
| | 60 | 40 | 8 | 150000 |
| 2A | 25 | 40 | 8 | 48000 |
| | 25 | 40 | 10 | 12000 |
| | 60 | 40 | 8 | 64000 |
| | 80 | 40 | 8 | 70000 |
| | 25 | 100 | 8 | 57000 |
| 2B | 25 | 40 | 8 | 80000 |
| | 60 | 40 | 8 | 135000 |
| | 25 | 100 | 8 | 260000 |

The results indicate that increasing the presence of sodium citrate decreases the elastic modulus of all gelled products. Further, the results indicate that increasing the amount of calcium present in general increases the elastic modulus of all gelled products.

-13-

The cans are opened and the contents visually inspected. In both cases, the meat matrix is gellified, retains its shape and has a firm texture.

-15-

7. A process according to claim 5 in which the comminuted vegetable matter is extracted by suspending it in an aqueous alkaline solution at a pH of 8 to 12 in the presence of 0.2 to 1% by weight of a sequestering agent and at a temperature of 5 to 50°C.
- 5 8. A process according to claim 6 or claim 7 in which the sequestering agent is a polyphosphate or citrate salt of a monovalent metal ion.
- 10 9. A process according to claim 5 in which the precipitate is neutralized in a suspension at a pH of 6 to 7.5 and alcohol is added to the suspension for precipitating the pectinaceous gelling agent.
- 15 10. A pectinaceous gelling agent obtained from vegetable matter containing pectinaceous substances having a degree of esterification of less than 50%, the gelling agent comprising 20% to 50% by weight of galacturonic acid and having a degree of esterification of 5% to 20% and obtainable by a process comprising:
- 20 subjecting comminuted vegetable matter to an acid or alkaline extraction in the presence of a sequestering agent for providing a pectinaceous extract;
- separating the extract from the vegetable matter;
- adjusting the pH of the extract to about 2 or less for causing a pectinaceous product to precipitate; and
- neutralizing the precipitate to provide the pectinaceous gelling agent.